Poster presentation

P37-From one-cation site model to binuclear cationic oxo-clusters in oxidative carbonylation of methanol over CuNaX zeolite

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Dimethylcarbonate (DMC) is one of green carbonylation/methylation agents and important fuel component with high oxygen content. The catalytic process of oxidative carbonylation on the Cu-form zeolites was studied herein as one of the possible alternatives instead of liquid-phase synthesis using corrosive solutions of CuCl [1,2]. Most authors accept that there are two steps in CH_3OH carbonylation, while the nature of intermediates is still under discussion. Zeroth kinetic order relative to oxygen concentration for DMC formation in three different Cu zeolites [3] points to probable Mars-van Krevelen mechanism in the opposite trend compared to liquid-state reaction in CuCl [1,2]. Regarding recently demonstrated oxidative activity of binuclear Cu_2O_x (x = 1, 2) [4] and trinuclear Cu_3O_3 clusters [5], participation of binuclear cationic $Cu(OH)_2Cu$ oxo-clusters has been admitted [6]. A three-stage carbonylation mechanism has been modelled using the PBE and PBEsol functionals within the projector augmented wave (PAW) method were performed with VASP [7]:

$$\{Cu^{+2}(OH)_2Cu^{+2}\}Z + CH_3OH \rightarrow \{Cu^{+2}(OCH_3)(OH)Cu^{+2}\}Z + H_2O \quad (1)$$

$$\{Cu^{+2}(OCH_3)(OH)Cu^{+2}\}Z + CH_3OH \rightarrow \{Cu^{+2}(OCH_3)_2Cu^{+2}\}Z + H_2O \quad (2)$$

$$\{Cu^{+2}(OCH_3)_2Cu^{+2}\}Z + CO \rightarrow \{Cu^{+2}(CH_3OCOOCH_3)Cu^{+2}\}Z \quad (3)$$

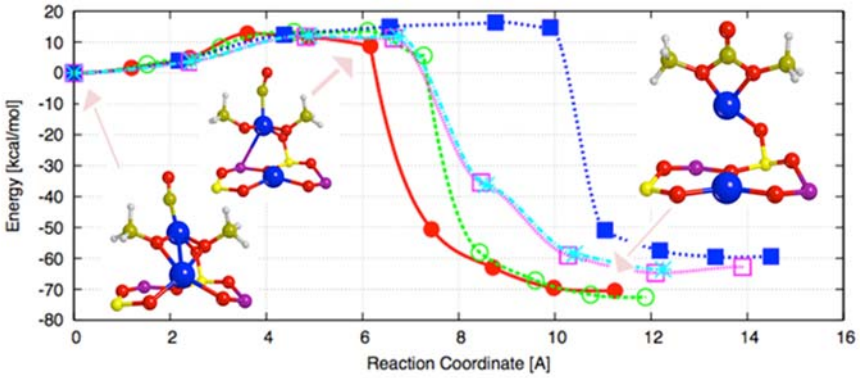

Fig. 1. Reaction coordinate (in Å) for CO attack over $Cu(OCH_3)_2Cu$ (3) in CuNaX obtained with different DFT functionals (PBE: closed circles, PBEsol: open circles) and using vdW corrections (PBE-D2: closed squares, PBE-D3(BJ): open squares, PBE-D3: stars) with periodic boundary conditions. The atomic colours are given in blue, red, yellow, magenta, olive, and grey for Cu, O, Si, Al, C, and H, respectively.

The results of the calculations using ciNEB algorithm [8] show that the step (3) is limiting one in agreement with experiment producing an activation barrier around 12–16 kcal/mol over CuNaX which is pretty close to the value 14.8 kcal/mol measured in CuY [3]. One believes that this route can be important for the Cu loadings when the concentration of binuclear copper clusters is essential.

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